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# Investigation of a method to hinder charge imbalance in the vanadium redox flow battery

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## HIGHLIGHTS

- A new concept to hinder charge imbalance in the vanadium redox battery is presented.
- A sensitive experimental method for determining catalytic activity is demonstrated.
- Hydrophobic coatings on the catalyst improved mechanical stability.
- Standard noble metal catalysts are shown to be effective.

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## ABSTRACT

In common with most aqueous batteries, the vanadium redox flow battery generates a small amount of hydrogen during operation. Over the lifetime of the battery this leads to a gradual imbalance in the state-of-charge (SoC) of the positive and negative electrolytes, with a consequent loss in discharge energy. To slow the rate of capacity fade to an acceptable level commercial vanadium redox flow batteries operate with a rather restricted maximum SoC. Increasing this SoC limit would improve the electrolyte utilisation, but also increase the rate of hydrogen evolution. Therefore a novel approach to alleviate this imbalance is examined, namely by reacting the evolved $H_2$, from the parasitic reaction at the negative electrodes, with the charged positive electrolyte. Due to the very slow native rate of reaction between $VO_2^+$ and $H_2$ at room temperature a series of potential catalysts are examined. Finely dispersed Pt, Ir and Pt–Ru on carbon paper are found to accelerate the reaction, with Pt–Ru being the most active.

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## 1. Introduction

A flow battery is a type of rechargeable energy storage device in which most of the electrolyte is contained in one or more tanks and flowed through electrochemical reactors during charge and discharge operations. In an early review Bartolozzi [1] distinguished between 'true' redox flow batteries (all electroactive species in solution) and redox-hybrid flow batteries (those involving solid metallic deposits and dissolved electroactive materials, e.g. the Zn–$Br_2$ system). Although it is now common to refer to both types as redox flow batteries, we will retain the definition of Bartolozzi in this work. Generally, redox flow batteries have been demonstrated with different elements for the positive and negative couples, such as the Fe–Cr battery, which was extensively developed by NASA in the 1970's [2–4] and several Japanese companies in the 1980's [5–7].

A microporous or ion-exchange membrane physically separates the positive and negative electrolytes in the electrochemical reactors. However, there is inevitably a gradual exchange of electroactive species through the membrane, which leads to a loss of capacity. In the case of redox flow batteries with dissimilar elements this leads to an irrecoverable loss of capacity [8–11]. For this reason batteries employing a single electroactive element in both electrolytes have been examined. Examples include the all uranium [12,13], all neptunium [14,15] and, the more commercially relevant, all vanadium [16,17].

The vanadium redox flow battery (VRFB) employs vanadium sulphates in oxidation states 2–5 dissolved in ca. 2 M $H_2SO_4$. The VRFB has been shown to have almost unlimited cycle life, because the electrode reactions involve no phase change [18–20]. It has a relatively low energy density (roughly equal to that of lead-acid batteries), but is stable to deep discharges and the energy and power can be independently specified, by changing the electrolyte

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volume and number of cells, respectively. Therefore, the VRFB is seen as an attractive proposition for stationary applications with frequent cycling [21,22]. It is also often reported that the electrolytes do not degrade and so have indefinite lifetime [23,24]. However, in common with every practical aqueous battery, hydrogen is evolved as a parasitic reaction during charging, Eqn. (2) [25,26]. Under normal operating conditions there are virtually no parasitic reactions on the positive electrodes (e.g. $O_2$ or $CO_2$ evolution). Therefore, the reactions during charging may be summarised as:

Negative electrode $$V^{3+} + e^- \leftrightarrow V^{2+} \quad (1)$$

And $$2H^+ + 2e^- \leftrightarrow H_2 \quad (2)$$

Positive electrode $$VO^{2+} + H_2O \leftrightarrow VO_2^+ + 2H^+ + e^- \quad (3)$$

The SoC of the electrolytes is defined as the extent to which the useful battery reactions (Eqs. (1) and (3)) have gone to completion. The vanadium concentration is nominally equal in both electrolytes and so the SoC should also, ideally, be equal. In practice a slight imbalance may be wanted to compensate for mass transport through the membrane [27–29]. However, if Eq. (2) proceeds to a notable extent there will be an imbalance in the SoC of the two electrolytes, with the positive electrolyte being more oxidised than the negative. This will decrease the usable charge and hence energy capacity of the battery. Ultimately the capacity may be restored by chemically or electrochemically reducing the positive electrolyte until the positive and negative again have the same SoC. However, this process increases the operating and maintenance costs for a system and so should be avoided for as long as possible. In practice this has been recognised by VRFB manufacturers, who tend to restrict the maximum SoC that is allowed on charging, and thereby reduce $H_2$ evolution [30,31]. Observations with a commercial 10 kW, 100 kWh VRFB (Gildemeister Energy Solutions FB10/100) have shown that selection of suitable operating parameters alone can lead to <1% imbalance in the SoC of the electrolytes per year (unpublished results based on SoC determination of positive and negative electrolytes by visible spectroscopy). Therefore, this system can be operated for many years before a chemical or electrochemical rebalancing of the electrolytes is required. However, in order to make better utilisation of the electrolyte it would be advantageous to extend the usable SoC range, i.e. terminate charging at a higher SoC. This would cause an increased rate of hydrogen evolution per year and would therefore be impractical unless a viable method to prevent/hinder the imbalance could be implemented.

Various strategies have been considered in an attempt to reduce the rate of SoC imbalance in flow batteries generally. These include the use of:

1. An electrochemical rebalance cell to adjust the SoC of one electrolyte independently of the other until they are in balance [8,32].
2. Coating the carbon felt electrodes with metals with a high hydrogen overpotential [33].
3. Add other elements that undergo reversible redox reactions at potentials below that of the $V^{2+/3+}$ reaction (Eq. (1)) [34].

Method (1) was employed extensively in the NASA Fe–Cr flow battery. It has the drawbacks of requiring regular monitoring of the SoC of both electrolytes independently, drawing some electrical power from the battery for the rebalance process, and needing extra hardware (rebalance cell, SoC monitoring equipment, etc.). Although method (1) can be effective, if rather involved, method (2) has, to the best knowledge of the authors, not been demonstrated to significantly reduce $H_2$ evolution in the VRFB. The third method limits localised overcharging of the negative electrodes by extending the charge capacity of the negative electrolyte in comparison to the positive. This technique is unlikely to reduce gas evolution in cases where the flow of electrolyte and homogeneity of electrode microstructure is sufficient to prevent localised overcharging *per se*. It is observed that some $H_2$ evolution occurs concurrently with the required electrode reactions even when there is no overcharging [35].

This work investigates the possibility of reducing charged positive electrolyte with evolved $H_2$ and hence keeping the SoC of the two electrolytes in balance, Eqn. (4). This concept is shown schematically in Fig. 1. The reduction may alternatively be considered, at least on a solid catalyst, as hydrogen dissociation, Eq. (2), together with reduction of $VO_2^+$ according to Eq. (3).

Proposed rebalance reaction $$VO_2^+ + H_2 \rightarrow VO^{2+} + H_2O \quad (4)$$

To prevent the need for complex monitoring and control hardware it was decided to combine the gas headspace of the two tanks and insert a catalytic element in contact with the positive electrolyte and gas volume. Judicious catalyst selection should then ensure passive rebalancing of the electrolytes.

## 2. Experimental

### 2.1. Equipment to determine catalytic activity

In order to examine the effectivity of various catalysts to enhance the rate of the reaction in Eq. (4) a test system was

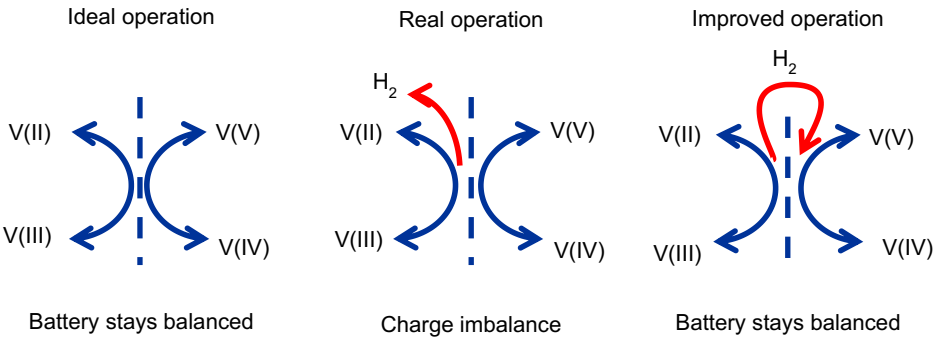


**Fig. 1.** Schematic representation of the proposed catalytic rebalance concept.

constructed as shown in Fig. 2. Positive and negative VRFB electrolytes were pumped, at ~20 ml $min^{-1}$, using small, magnetically-coupled centrifugal pumps through an electrochemical cell and back into the respective compartments of the tank, Fig. 2a. The electrochemical cell consisted of a carbon felt electrode in both reaction chambers separated by an ion exchange membrane of 20 $cm^2$ exposed area. A potential difference of 1.75 V was applied continuously to the cell in order to charge the electrolytes.

Fig. 2b shows detail of the tank. The two electrolytes are divided by a partition wall, but the gas headspace is common to both. The burst valve and flame arrestor are safety devices employed to mitigate the danger of working with potentially explosive gas mixtures. The oil-filled gas bubbler limits over or under pressure in the tank, but is insufficient to handle very rapid changes in gas pressure. Inlets and outlets for the electrolytes were placed at opposing corners of the respective tank sections. In addition PTFE-coated stir bars were rotated (at ca. 200 rpm) magnetically, to prevent stratification of the electrolytes. This measure was visibly effective in that the positive electrolyte had a uniform colour through the tank, at any given SoC.

$H_2$ concentration in the space over the electrolyte was measured by an explosion-protected HPS-100 sensor from Applied Sensor, that covers a 0%–100% range, and recorded by microcomputer.

The tank chambers were initially filled with 500 ml of electrolyte on each side, such that the enclosed gas volume was 4500 ml. The electrolyte initially had the same composition in both chambers, namely; an aqueous solution of 2 M $H_2SO_4$, 0.8 M $VSO_4$, 0.4 M $V_2(SO_4)_3$ and 0.05 M $H_3PO_4$ (to hinder precipitation of $V_2O_5$ from charged positive electrolyte).

A disc of hydrophilic, microporous polypropylene was stretched over an elastomeric O-ring to form a raft, which was fixed in the positive electrolyte chamber of the tank, such that the microporous sheet was ca. 1 mm below, and parallel to, the electrolyte surface, Fig. 2c. The O-ring was of sufficient height that electrolyte could only enter or leave the raft through the microporous layer, which served as a support to the catalyst under test. The microporous layer was necessary to prevent fragments of the, sometimes rather fragile, catalysts from entering the electrochemical cell. This configuration was selected after experimental optimisation, because it presented the best access to electrolyte and gas to the catalyst, with the least risk of flooding or dehydrating.

All experiments were run at room temperature, 24 ± 2 °C.

The three different noble metal catalysts; Pt, Pt–Ru (roughly 40 at% Ru by EDX) and Ir, on a carbon paper support were purchased from Baltic Fuel Cells GmbH (Schwerin, Germany). The noble metals had an area loading of 2.5 mg $cm^{-2}$ and were supplied with and without a hydrophobic fluorinated polymer microporous layer. From scanning electron microscopy (FEI Quanta 200 microscope,

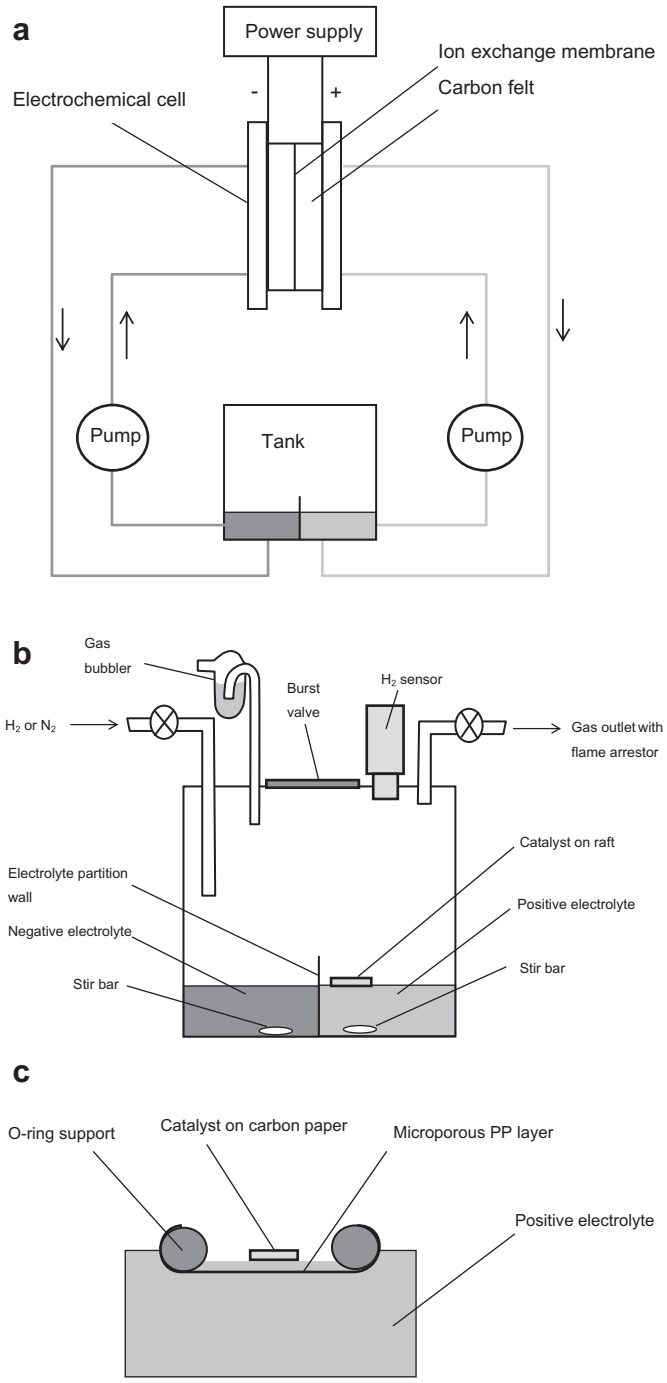


**Fig. 2.** Schematic illustration of the apparatus used in the evaluation of catalyst performance for the reduction of positive vanadium electrolyte with $H_2$, a) system, b) detail of the tank, c) detail of the catalyst and raft.

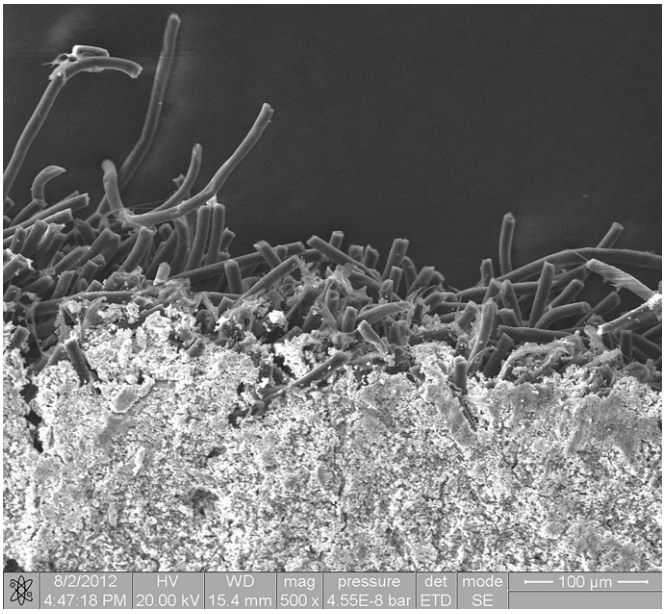


**Fig. 3.** Scanning electron micrographs of a cut edge of a catalyst containing a supported Pt–Ru catalyst layer on carbon paper without a hydrophobic layer. Note that the catalyst layer is one face of the carbon felt only.

operated at CEST GmbH) it was observed that the catalyst layers were on one face of the carbon paper only, Fig. 3. The gas diffusion electrodes were placed on the raft, Fig. 2, such that the face coated with noble metal particles was downwards, in contact with the electrolyte. However, the electrodes were not completely submerged in the electrolyte so the back face was exposed to the surrounding gas.

The catalysts with hydrophobic treatment were similar except that the carbon fibres were partially coated with fluorinated polymer. These materials were originally developed as gas diffusion electrodes for fuel cells where they would be expected to operate at ~80 °C and had not been optimised for the current application.

### 2.2. Test procedure

Prior to testing the catalysts the electrolyte was charged until the positive electrolyte was transparent and orange in appearance. This corresponds to an SoC of ~100%, or, in other words, the average oxidation state of V in the positive electrolyte was ~5. Aerial oxidation of V(II) caused an imbalance in the SoC between the two electrolytes, and vanadium in the negative electrolyte at the end of charging had an average oxidation state between 2 and 3.

The cell was held potentiostatically at 1.75 V during all of the following experiments to ensure full oxidation of the positive electrolyte. Therefore, the current was limited by the concentration of V(IV) in the positive electrolyte and not by the negative electrolyte.

Samples of the catalyst-loaded gas diffusion electrodes were cut to typically 6.3 $cm^2$ area and placed in the raft, where they floated on a thin layer of positive electrolyte. The upper lid of the tank was then sealed and the tank flushed with excess $N_2$ to reduce the $O_2$ concentration. The $N_2$ flow was stopped and pure $H_2$ pumped through the tank until a pre-defined concentration was reached. At this point the tank was isolated from the gas supply and exhaust by hand valves. After a pre-determined time (typically 3300 s), the valves were opened and the tank again flushed with $N_2$ until the measured $H_2$ concentration was <0.5%. Measurement of $H_2$ concentration and current through the electrochemical cell proceeded from the time the tank was closed until either 1 h after purging out the $H_2$ or until the current through the electrochemical cell returned to the initial value, whichever was longer.

Any increase in the cell current is taken to be due to the reactions given in Eqs. (1) and (3), which are limited by the $VO^{2+}$ concentration. In turn $VO^{2+}$ can be formed through either crossover of vanadium ions through the membrane or reduction of $VO_2^+$ by $H_2$, Eq. (4). Even after fully charging the positive electrolyte a small but relatively stable current flowed through the electrochemical cell (for example ca. 3.5 mA in Fig. 4). This is due to crossover of vanadium species through the ion-exchange membrane.

Therefore, this technique provides a sensitive measure of the reduction reaction and its enhancement through catalytic agents. Current may be seen to be much more sensitive parameter than $H_2$ concentration to the catalytic activity by a simple example: increase in the cell current by 1 mA for 1 h is easily discernible; however, this would correspond to a decrease in the $H_2$ concentration in the tank of only 0.01% in 1 h, which is much below the change caused through leakage (ca. 4% $h^{-1}$ at 80% $H_2$ concentration).

## 3. Results & discussion

Neither the electrochemical cell current nor the colour of the charged positive electrolyte was found to change in response to exposure to >80% concentration of $H_2$ for 3600 s. Therefore, given a gas to electrolyte contact area of 130 $cm^2$ the uncatalysed reaction rate was $<2.2 \times 10^{-8}$ mol $VO_2^+$ $cm^{-2}$ $h^{-1}$, which may be considered

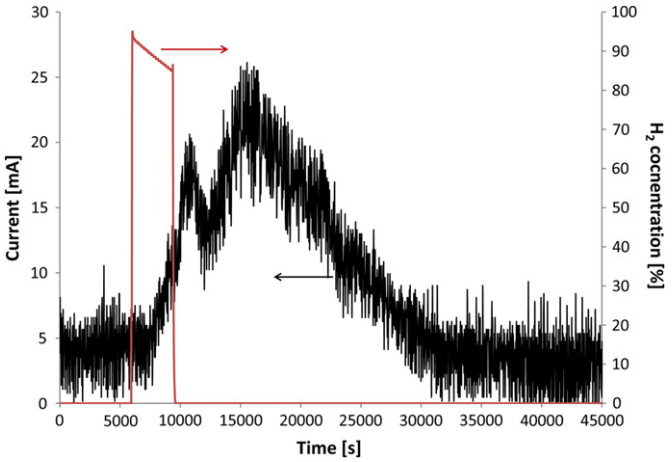


**Fig. 4.** The cell current, measured for a 6.3 $cm^2$ area carbon paper with 2.5 mg $cm^{-2}$ loading of Pt–Ru catalyst in contact with charged positive vanadium electrolyte, together with hydrogen concentration in the gas space arranged against time.

in terms of an equivalent current density of <8 μA $cm^{-2}$ (electrolyte-gas contact area). The equivalent current density is calculated from the amount of excess $VO^{2+}$ produced when $H_2$ is present, assuming the reduction to have proceeded through the electrochemical reaction given in Eq. (3).

In contrast the cell current with a 6.3 $cm^2$ Pt–Ru on carbon paper catalyst is shown in Fig. 4. An $H_2$ concentration of ~90% was maintained for 3660 s. The slight decrease in $H_2$ concentration over this period was mainly attributed to leakage from the system as mentioned above. However, during the exposure time the electrolyte became significantly darker, as is typical for positive electrolyte at <100% SoC. This observation alone is enough to identify Pt–Ru as having vastly accelerated the reduction of $VO_2^+$. However, visible spectroscopy of V(IV) solutions in sulphuric acid containing concentrated $VO_2^+$ does not follow the Beer-Lambert relationship due to the formation of highly absorbent complexes containing both V(IV) and V(V) [36,37]. In contrast current through the electrochemical cell is a sensitive and quantitative measure of the reduction reaction. Therefore, the electrochemical method was preferred for quantitative analysis of the reaction.

Although the current increased within the period of $H_2$ exposure, exhaustive electrolysis required considerably longer at ca. 23,000 s. Therefore, for comparative purposes it is convenient to calculate an equivalent catalytic current, $i_{cat}$, as:

$$i_{\mathrm{cat}} = \frac{\int_{t_0}^{t_1} i - i_0 \mathrm{d}t}{(t_2 - t_0)} \quad (5)$$

Where $t_0$ and $t_2$ are the time when the $H_2$ is first introduced into the system and the time when the level is below the detection limit (0.5%), respectively. Electrolysis is taken to be complete at $t_1$, the time when the current, $i$, returns to the original level, $i_0$. Therefore, the numerator is the charge passed as a result of oxidation of $VO^{2+}$, which was formed through the catalytic reduction of $VO_2^+$ by $H_2$.

From Fig. 4 it may be seen that the initial current, $i_0$ ~ 4 mA and after 45,000 s the current returned to a slightly lower value. The non-zero current is due to vanadium species crossing the ion exchange membrane from the negative to positive electrolytes. Numerically the minor differences in $i_o$ were caused by changes in the ambient temperature over the long timescale of these experiments (vanadium transport through the ion exchange membrane is

strongly temperature dependent). Therefore, an average value of $i_o$ was used in Eq. (5).

It is possible that the reduction rate is limited by diffusion of vanadium species through the microporous polypropylene membrane. To examine this possibility several samples of Pt–Ru on carbon paper of different size (up to 6.5 $cm^2$) were independently tested in the same raft (with a membrane area of 7.0 $cm^2$). The catalytic current was found to be linearly dependent on the sample area, Fig. 5. However, if diffusion through the membrane had been limiting $i_{cat}$ would be expected to be independent on the geometric electrode area, $A$. Therefore, the membrane did not limit the reaction rate in these experiments and it is reasonable to compare catalysts in terms of the equivalent catalytic current density $j_{cat}$ where $j_{cat} = i_{cat}/A$.

Also from Fig. 5, for the Pt–Ru catalyst, $j_{cat}$ = 19.1 mA $cm^{-2}$ in a 90% $H_2$ atmosphere (ca. 3300 s exposure). This is >2500 times faster than the uncatalysed reaction rate at room temperature. Practically, in a VRFB, it would also imply that 1 $cm^2$ of the catalyst could react with up to 190 ml of $H_2$ per day.

All three types of noble metal catalysts were found to increase the reaction rate, Fig. 6. The microporous hydrophobic layer did not significantly affect the reaction rate, although it made the electrodes more physically stable and less liable to shed material on handling. The noble metals were increasingly active in the order Pt < Ir < Pt–Ru.

At least one catalyst of each type was tested on consecutive days, after remaining in contact with the charged positive electrolyte for ≥24 h in the absence of hydrogen. The Pt and Pt–Ru catalysts gave reproducible results on the second day. However, the Ir catalyst showed no activity after 24 h contact with the electrolyte. The loss in activity is most likely due to oxidation of the Ir. The standard electrode potentials for oxidation of Ir to $Ir^{3+}$ or $IrO_2$ (Eqs. (6) and (7) respectively) are close to the practical redox potential for the positive electrolyte given in Eq. (3), which is found experimentally at ~1.11 V vs. SHE for 85% SoC at 25 °C.

$$Ir \leftrightarrow Ir^{3+} + 3e^- \qquad E^o = 1.156 \text{ V vs. SHE} \qquad (6)$$

$$Ir + 2H_2O \leftrightarrow IrO_2 + 4H^+ + 4e^- E^o = 0.926 \text{ V vs. SHE} \qquad (7)$$

However, it is also possible that the catalytic activity was lost due to degradation of the support material, although no similar loss was observed for Pt or Pt–Ru. Therefore, the Ir catalyst although initially active is not sufficiently stable to be of practical application. The instability of the Ir catalyst may also explain the relative large observed variation in $j_{cat}$, which would have had a dependence on the, not always constant, contact time in electrolyte prior to $H_2$ exposure.

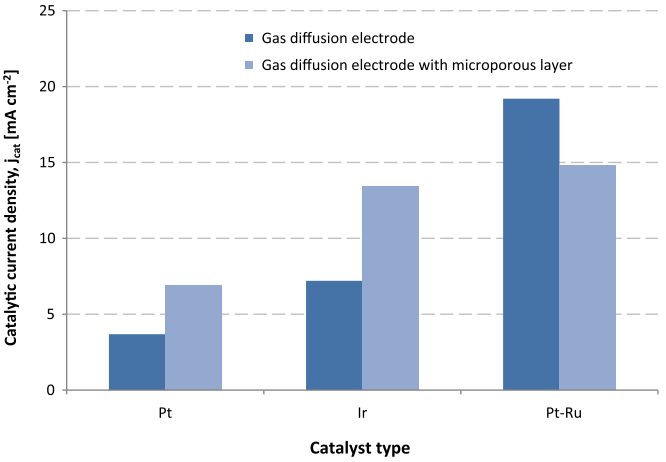


**Fig. 6.** Catalytic current density, as measured at room temperature on 3300 s exposure to 90% $H_2$ atmosphere, of 2.5 mg $cm^{-2}$ of noble metal catalyst on carbon paper (gas diffusion electrode) with and without a hydrophobic microporous layer.

The length of $H_2$ exposure was also varied as shown in Fig. 7 for a 6.3 $cm^2$ Pt–Ru catalyst. As can be seen the charge passed increased monotonically, but a linear regression fit exhibited a non-zero offset of catalytic charge passed (numerically equal to 15.6 C $cm^{-2}$) for zero exposure time. This probably arises from a reaction rate dependence on the local $VO_2^+$ concentration at the catalyst surface, which would fall initially until a pseudo-steady state has been reached. The reaction rate dependence on $VO_2^+$ concentration was not addressed in this work. However, the influence of $H_2$ concentration was investigated. By varying the average $H_2$ concentration and maintaining an exposure time of ca. 3300 s it was found that $j_{cat}$ remained constant for a Pt loaded catalyst from 8% to 83% $H_2$. Therefore, at least under these conditions, the reaction was zero-order with respect to $H_2$. Practically this is significant, although it is preferred to ensure lower $H_2$ concentration in the electrolyte tank headspace. This would reduce

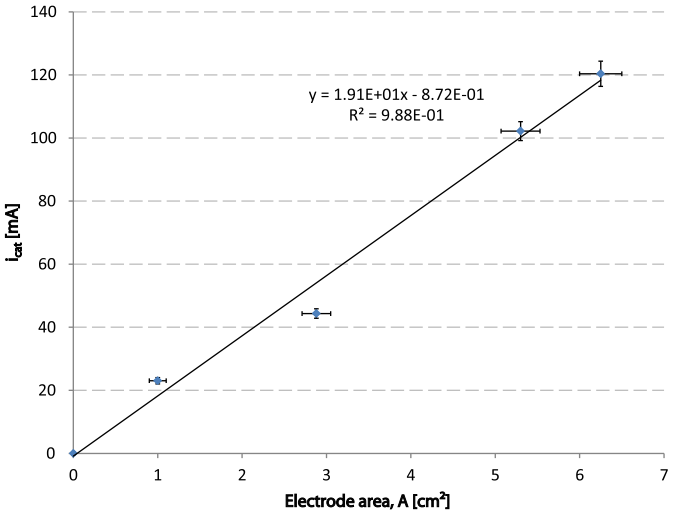


**Fig. 5.** Catalytic current resulting from reduction of positive vanadium electrolyte with $H_2$ arranged against geometric area of the Pt–Ru catalyst-loaded carbon paper and a linear regression curve.

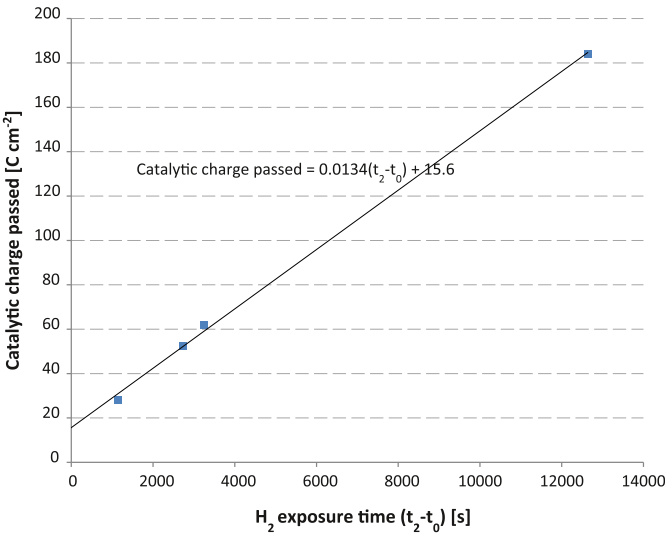


**Fig. 7.** Catalytic charge passed for a Pt–Ru catalyst-loaded carbon paper of 6.3 $cm^2$ geometric area arranged against $H_2$ exposure time.

the rate of $H_2$ loss from the system, which may be assumed to increase proportionally to the $H_2$ concentration, and hence hinder the rate of SoC imbalance. Therefore, in further work, it would be of value to understand the rate of reaction at $<8\%$ $H_2$. Nevertheless, through monitoring of more than 20 commercial systems in the field, it has been observed that $H_2$ concentrations in the range $\geq 8\%$ can arise, even with rather low gas evolution rates, after several months of operation.

## 4. Conclusions

In order to hinder capacity fade in the vanadium redox flow battery, especially if the rate of $H_2$ evolution is increased by raising the maximum permissible SoC, a novel rebalance concept was examined. An experimental apparatus for determining the rate of reaction between $H_2$ and charged positive VRFB electrolyte has been demonstrated. However, the reaction rate is very slow at room temperature without the use of a catalyst.

Pt, Ir and Pt–Ru were tested and found to be effective catalysts at 2.5 mg $cm^{-2}$ loading on a non-woven carbon support. The additional use of a microporous hydrophobic layer increased the mechanical stability but did not significantly alter the catalyst performance. Of the catalysts tested Ir lost its catalytic action, presumably through oxidation in the acidic V(V) solution, within 24 h. Pt-Ru was the best catalyst with an increase in reaction rate of $>2500$ over the non-catalysed system.

Although more effort is required to demonstrate safety and stability in practical applications, this work demonstrates proof of concept for a novel method to extend the electrolyte utilisation in the VRFB and/or electrolyte lifetime before rebalancing.

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